

(NASA-CR-196769) HIGH TEMPERATURE  
SUPERCONDUCTING FILMS ON INSULATING  
SUBSTRATES Final Technical Report  
(Oberlin Coll.) 5 p

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## 1. Project Summary

This is the final technical report for NASA contract number NAG 3-885, *High Temperature Superconducting Films on Insulating Substrates*. The contract was funded for three consecutive, one-year periods beginning on March 15, 1988 and ending on March 14, 1991, for a total funding amount of \$100,000. Funding for the first year of the contract was \$50,000, while funding for the subsequent two years was \$25,000 each. The principal investigator for the research was Dr. John H. Scofield, Asst. Professor of Physics at Oberlin College. The contract also supported several research assistants, all students at Oberlin College. These were: Lou Bajuk ('89), Joe Peidel ('89), Steve Klein ('89), and Matt Trawick ('91). 2157-12 22276 5P

During the period of the research contract, a vacuum system was designed, assembled, and used to co-evaporate thin films of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  from copper (Cu), yttrium (Y), and barium-fluoride ( $\text{BaF}_2$ ) sources on a variety of substrates. In total, 82 separate depositions were performed onto an estimated 200 substrates. Substrate materials included glass microscope slides, oxidized and unoxidized silicon wafers, sapphire ( $\text{Al}_2\text{O}_3$ ), yttrium-stabilized zirconia (YSZ), magnesium-oxide ( $\text{MgO}$ ), strontium-titanate ( $\text{SrTiO}_3$ ), lanthanum-gallate ( $\text{LaGaO}_3$ ), and lanthanum-aluminate ( $\text{LaAlO}_3$ ). As deposited films were insulating, requiring a post-deposition oxygen anneal to achieve the desired  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , superconducting compound. Not surprisingly, the best quality superconducting films (i.e., sharp superconducting transitions near 93 K with high critical current densities) were achieved on  $\text{SrTiO}_3$ ,  $\text{LaGaO}_3$ , and  $\text{LaAlO}_3$  substrates.

The Oberlin work concentrated on the fabrication of superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_7$  films [1,2], supplying films to NASA collaborators (S. Alterovitz and M. Stan) and collaborators at the University of Rochester (W. Donaldson's group). Auger composition analysis was performed on several films by Ali Dayem and Eric Westerwick at AT&T Bell Laboratories. The reproducibility of film composition became the focus of our work during the third year of the contract. Ultimately it was decided that the spatial variation of the evaporant was simply too great to achieve reproducible results (see below).

The University of Rochester group conducted experiments on the laser-induced, thermal switching of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  films [3-5]. During the last phase of this work, we performed measurements of 1/f noise in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  in both the normal and superconducting state [6].

## 2. Sample Fabrication

## 2.1 Co-evaporation System

The Y, Cu,  $\text{BaF}_2$  co-evaporation process was first developed at AT&T Bell Laboratories by myself and coworkers [1]. At Oberlin, the co-evaporation process was implemented in a vacuum system consisting of a 24-in. stainless steel bell jar evacuated with a Varian 6 in. diffusion pump/liquid nitrogen cold-trap stack.  $\text{YBa}_2\text{Cu}_3\text{O}_7$  films were obtained by exposing substrates to simultaneous molecular beams of oxygen ( $\text{O}_2$ ), copper (Cu), yttrium (Y), and barium-fluoride ( $\text{BaF}_2$ ). Originally, the Cu and Y beams were created from molten metal sources using two Sloan model BXV-6, 7 cc, single-pocket, 180-deg. e-guns and a Sloan model Six/Ten, dual e-gun power supply. The  $\text{BaF}_2$  beam was obtained through sublimation of  $\text{BaF}_2$  chunks held in a resistively

heated, tungsten boat.<sup>1</sup> During the last year of the research contract, much of our work focused on improving beam control from the three sources (see below). The 0-200A evaporation boat current is furnished by the secondary of a 2kVA filament transformer. The O<sub>2</sub> flux is obtained by maintaining a high partial pressure of oxygen gas in the vacuum station. Oxygen is admitted into the station through a narrow tube located near the substrate. The pressure near the substrate is substantially higher than that elsewhere in the station. The pressure measured near the base of the bell jar is typically in the mid 10<sup>-6</sup> Torr range.

The Cu, Y, and BaF<sub>2</sub> sources are each operated in closed loop feedback control with a three independent Inficon model XTC quartz crystal deposition rate controllers, each providing a 0-10 VDC control signal that is fed back control the temperature of the appropriate source. The Sloan Six/Ten e-gun power supply is configured to use such a signal to control filament current to each of the e-guns. We designed and constructed an SCR, high-current switching circuit to control the primary current the filament transformer that powers the BaF<sub>2</sub> evaporation boat [2]. This allows the individual molecular fluxes to be controlled, as well as the Y:Cu:Ba mixing ratio.

The three sources were arranged in an equilateral triangle (side length of 8 in.) with the substrate centered about 16 inches above the plane of the sources. Simple geometry calculations showed that each of the molecular beams spreads in such a way as to yield about a 5% variation in flux across the 2 in. diameter substrate holder.

Auger composition analysis on samples from successive depositions were used to determine deposition rates for achieving the 1-2-3 compound. Optimal results were achieved with the Y deposition rate set to 0.31 nm/s, the copper to 0.41 nm/s, and the BaF<sub>2</sub> set to 0.88 nm/s. According to the deposition rate monitors, temporal fluctuations in the Y and Cu deposition rates were typically 0.03 nm/s, while fluctuations in the BaF<sub>2</sub> were significantly larger, typically 0.2 nm/s. The fluctuations average to zero, so that at the end of a typical deposition, the integrated rates (i.e., final thicknesses of the constituent parts) were within 1% of the desired ratios. During the last year of the contract we discovered that the spatial distribution of the flux from the sources was time-dependent, and that it varied during from run to run and also during a particular run. This problem ultimately resulted in the suspension of the work (see below).

## 2.2 Oxygen anneal

As deposited films were dark brown, semi-transparent and insulating. These films were subsequently annealed in flowing wet oxygen at 875°C for about one hour, then cooled in flowing dry oxygen at a rate of about 50°C/min. Films so annealed were black, opaque, and had room temperature resistivities ranging from (1-10) x 10<sup>-3</sup> ohm-cm. Films deposited on SrTiO<sub>3</sub> or YSZ substrates always exhibit superconductivity with transitions onsets at 90 ± 3 K. For the deposition parameters given above, films deposited on SrTiO<sub>3</sub>, LaGaO<sub>3</sub>, or LaAlO<sub>3</sub> typically reached zero resistance at a temperature above 87K; some samples reach zero resistance above 90K. Films deposited on YSZ substrates tended to achieve zero resistance at somewhat lower temperatures, usually from 80K to 87K.

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<sup>1</sup> In the last year of the contract the Cu and BaF<sub>2</sub> sources were interchanged so that Cu was evaporated from the thermal boat and BaF<sub>2</sub> from an e-gun.

### 2.3 Reproducibility Problems

During the third year of the research contract it became painfully obvious that films were not very reproducible. Films, nominally fabricated under identical conditions (i.e., evaporation rates) exhibited different properties, especially in their critical current densities. We investigated two possible causes for variation in the film properties: 1) high water partial pressure in the vacuum system during deposition due to outgassing associated with heating of the BaF<sub>2</sub> evaporation source, and 2) temporal variation in the spatial distribution of evaporant. Both of these issues were important.

#### 2.3.1 Outgassing

In its original configuration, the barium fluoride source consisted of a small, open tungsten boat filled with BaF<sub>2</sub> chunks. As mentioned above, the barium fluoride deposition rate suffered from large temporal fluctuations. Moreover, film thicknesses were ultimately limited by the amount of BaF<sub>2</sub> that the small boat could hold, typically a few thousand angstroms. Thicker films could be deposited if we used a larger BaF<sub>2</sub> boat. In addition, it was decided to change from an open evaporation boat to an indirect oven (such as that used to evaporate silicon monoxide) achieve a more constant deposition rate.

The BaF<sub>2</sub> source upgrade achieved both of the desired effects, but resulted in the station pressure climbing during deposition. The new evaporation source, being larger, required more current, and accordingly, dissipated much more heat than the smaller source. Neighboring components of the vacuum system quickly heated up, resulting in significant outgassing and an increase in H<sub>2</sub>O pressure in the chamber.

To reduce outgassing, a stainless steel radiation shield was designed and installed around the BaF<sub>2</sub> source. While reducing the problem, the problem remained significant. It was subsequently discovered that the copper, electrical feed-throughs to the resistively-heated BaF<sub>2</sub> source were getting too hot to touch, and were in danger of compromising their O-ring seals. These feed-throughs were subsequently replaced with water-cooled copper feed-throughs.

With the installation of the larger BaF<sub>2</sub> source, the radiation shield, and the water-cooled feed-throughs, the BaF<sub>2</sub> rate was stabilized, but outgassing remained significant. Heater tapes were wrapped around the outside of the chamber walls. A procedure was developed for baking the chamber while pumping for about 24 hours before deposition. The system was allowed to outgas with the chamber wall raised to near 100 deg. C, and all three sources raised to just below evaporation temperature. This procedure reduced outgassing to a tolerable level, but the problem remained significant, and, due to the long pumping times, sample turnaround was greatly limited.

In the end, this source configuration was rejected and instead, the BaF<sub>2</sub> and Cu sources were interchanged. The BaF<sub>2</sub> was placed in one of the e-guns, and the Cu was evaporated from a boat. This solved the outgassing problem and allowed for thicker film deposition, since a) Cu was evaporated from the thermal boat with much less power dissipation, and b) the e-gun hearth could hold relatively more BaF<sub>2</sub> than the small thermal boat.

#### 2.3.2 Improved e-gun rastering

Having overcome the above problem, we still found film composition to be quite irreproducible. Inspection showed that the electron beam sources were not being rastered significantly so that the source developed a "crater" where the e-beam was

focused during deposition, possibly leading to non uniformity in the spatial distribution of the evaporant. This was especially noticeable once we began to evaporate BaF<sub>2</sub> from an e-gun. Note that the Sloan e-guns are able to raster the e-beam only along one axis, with beam width determined by dispersion from the 0.5-cm long e-gun filament. To improve rastering, the Sloan's sweep circuit was disabled (for both guns) and an external triangular waveform (with DC offset) was connected to the focusing magnet of each gun. The triangular sweep voltage was supplied by a Wavetek model 157 frequency synthesizer connected to a Lambda model LMF-7-M-Y DC power supply; the latter supplying the DC offset required to bend the e-beam in the center of the hearth. Independent circuits were devoted to each of the two e-guns. The BaF<sub>2</sub> magnet was rastered with a frequency of 4 Hz while the Y e-gun was rastered at 8 Hz.

### 2.3.3 *Temporal variation in Spatial Distribution of Evaporant*

One tacit assumption in using the XTC deposition rate controllers was that the flux of evaporant at the substrate, while not equal to, at all times was proportional to the flux recorded at the sensor, located some distance away from the substrate. Proper feedback control does not require that the spatial distribution of evaporant be symmetric, it only requires that the spatial distribution not vary in time. (The flux may vary in time, but in such a way that the ratio of the flux at the substrate to that at the sensor be independent of time, i.e., the two must track each other.) The spatial distribution of evaporant depends on the shape of the source in the e-gun or thermal boat. Visual inspection showed that the Y charge, for instance, had a different shape before each deposition, suggesting that the ratio of the Y-flux at the substrate to that at the Y-sensor might not be the same at the beginning of each run.

To test this hypothesis and to provide for better deposition rate calibration, a fourth crystal deposition rate sensor was installed on the shutter in front of the substrate stage. With only one source evaporating, it was possible to monitor the ratio of the flux at the substrate (shutter) to that at the crystal sensor normally used to monitor the deposition rate for that source. Our hope was that this ratio would be relatively constant during a particular deposition (i.e., over time scales of minutes) though it might vary slowly from run to run as the shape of the charge slowly changed (i.e., time scales of hours). Had this been the case, we planned to develop a calibration scheme to use crystal sensor on the shutter to individually re-calibrate each of the three deposition rates just before each deposition. A similar procedure had proved successful elsewhere.<sup>2</sup>

The above test was performed for each of the three individual sources: Cu evaporated from a boat, Y from one e-gun, and BaF<sub>2</sub> from the other e-gun. We discovered that the spatial distribution of both the Cu evaporant and the Y evaporant remained quite constant in time. In contrast, the distribution of the BaF<sub>2</sub> evaporant varied significantly with time. Specifically, we discovered that the ratio of the deposition rate at the BaF<sub>2</sub> sensor to the rate at the shutter sensor varied by nearly 15% over a period 10 minutes (with only BaF<sub>2</sub> being deposited at a typical deposition rate, of 0.9 nm/s)! This explained why we could not achieve consistent film stoichiometry.

This problem was never solved. I concluded that, without major modification to the rastering system, the Sloan e-guns were simply not of sufficient quality to perform coevaporation with 2% or better control of stoichiometry.

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<sup>2</sup> Improved control over film stoichiometry has been achieved by the Bell Labs group by instituting such a calibration procedure according to R. Howard.

### 3. 1/f Noise Experiments

In addition to supplying films to other groups, one experiment was conducted at Oberlin on the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  films -- the measurement of their 1/f noise. For 1/f noise and  $j_c$  measurements,  $\text{YBa}_2\text{Cu}_3\text{O}_7$  microbridges were formed with photolithography and liftoff following deposition, and prior to annealing. Using this technique, superconducting microbridges were formed having widths smaller than 10 microns. The  $R=0$  temperatures of microbridges so fabricated were about 60K, lower than that for unpatterned films.

Resistance fluctuations of two  $\text{YBa}_2\text{Cu}_3\text{O}_7$  microbridges were measured in their normal states for temperatures from 50 to 300K [6]. The resistance,  $R$ , of one sample was found to fluctuate with a power spectral density  $S_R(f) = C/f^\gamma$ , where  $C$  is the noise magnitude and  $\gamma$  is the frequency exponent. The noise level  $C$  was largest at room temperature and decreases linearly with  $T$  down to 93K. Between 93K and 60K measurements are unstable as the sample is neither superconducting nor Ohmic. Below 60K the film is superconducting and the 1/f noise is not measurable with our instrumentation. The frequency exponent  $\gamma = 1.20$  and was nearly constant over the entire range of temperature. As has been found for so many properties, we believe that the 1/f noise of these  $\text{YBa}_2\text{Cu}_3\text{O}_7$  microbridges is dominated by extrinsic defects (especially those associated with grain boundaries) and is not intrinsic to the material. Thus, this line of inquiry was suspended until better quality films could be fabricated.

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